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Progress Report for N00014-97-1-0745
Electron Energy Levels in Magnetic Nanoparticles
Daniel C. Ralph, Cornell University

1. Summary of Progress for the Period 6/1/97-4/30/98

The goal of this project is to fabricate and investigate tunneling transistors made surrounding a single nm-scale ferromagnetic particle, a particle small enough to permit the study of electron tunneling via the individual quantum energy levels inside the particle. The motivation is to use these devices as a kind of microscope, to understand the processes which govern the operation of magnetic tunneling devices on both the nanometer scale and larger scales. The ability to manipulate electron flow through individual quantum levels provides the experimental advantages that these levels should be maximally spin-polarized in a ferromagnetic nanoparticle, thus allowing more controlled studies of spin-polarized tunneling than are possible in larger devices which have a continuum density of states, and also that transitions between individual eigenstates may be investigated in order to understand the electron energy-loss mechanisms and non-equilibrium phenomena which are central to the properties of tunneling devices under bias. Investigation of the overall spectra of energy levels, and how they change as a function of external magnetic field, should also yield new information about the nature of the interactions between electrons inside a ferromagnet, and the processes of magnetization reversal in single magnetic particles.

The first several months of the grant period were spent completing the installation of the three major pieces of equipment needed to carry out the project. All of this apparatus is now in place and is fully functional. **(1) Oxford Kelvinox 100 Dilution Refrigerator:** This is designed for fast turn-around times for looking at many samples, with a home-made, electromagnetically-shielded sample stage and low-temperature electrical filters needed to do sensitive spectroscopic measurements. We have made measurements at temperatures below 15 mK, and in magnetic fields up to 9 Tesla. **(2) Vacuum evaporation system for metal depositions:** This contains a 4-hearth electron beam evaporation source, 2 thermal evaporation sources, and facilities for vacuum anodization, which provide all the flexibility that we require for fabricating our magnetic devices. We have constructed a rotating sample holder, and a sample stage for liquid-nitrogen-cooled evaporations. **(3) 1 degree Kelvin dipper cryostat with 3 Tesla magnet:** This is a system for quick characterization of samples. The cryostat and the magnet both fit through the throat of a helium storage dewar, so no helium transfers are required. All of the electrical connections and computer software needed for data acquisition have been assembled and written.

As an initial test of our processes for device fabrication and measurement, and as a starter project for the students, we have fabricated nm-scale tunneling devices made with single superconducting aluminum particles containing 4% gold impurities. We then measured the discrete electronic spectrum in the nanoparticle as a function of magnetic field, to study the effects of spin-orbit scattering from the impurities on the superconducting transition in the aluminum. This work is an extension of a project I performed as a postdoc in Prof. M. Tinkham's group at Harvard, where we measured the electronic states in aluminum nanoparticles without impurities. A selection of our new results is shown in Fig. 1. Tunneling peaks due to discrete quantum energy level in the nanoparticle are clearly visible, indicating that our fabrication and measurement set-ups are in good shape. In comparison to previous measurements on nanoparticles without impurities, the energy levels in the new work have a much weaker magnetic-field dependence. The effective g-values are in the range of 0.4 to 0.5, compared to approximately 2.0 for pure aluminum. This can be understood as a consequence of spin-mixing induced by spin-orbit scattering from the Au impurities. The magnitude of the superconducting gap in the nanoparticle is not significantly affected by the impurities,

which is expected because spin-orbit scattering does not break time-reversal symmetry. The energy levels in the sample with Au impurities can be seen to exhibit avoided crossings as a function of magnetic field, another consequence of spin-mixing. On account of the avoided crossings, the destruction of superconducting correlations is a gradual process in the samples with Au impurities, whereas it appears to come suddenly by means of a simple level crossing in pure Al nanoparticles. These measurements and related analysis were reported by a student, David Salinas, at the 1998 APS March Meeting.

In parallel with these experiments, we have begun working on optimizing the new fabrication procedures which are required for making the sort of device that is our primary interest -- nm-scale tunneling transistors containing a single ferromagnetic nanoparticle such as cobalt. The key step is to make reliable and reproducible nm-scale tunnel junctions between magnetic electrodes, with sufficiently low resistance to give a measurable current. The difficulty is that native oxides of ferromagnetic materials do not make appropriate tunnel barriers, unlike the aluminum oxide that we have used in previous work. We are pursuing two separate strategies, beginning in each case by studying simple tunnel junctions, rather than more complicated devices containing nanoparticles. In neither case are the initial results yet fully satisfactory, but I will show that the work has begun. One strategy is to use deposited barrier materials. A popular process used by groups making larger-area magnetic tunnel junctions is to deposit a thin film of aluminum onto the magnetic electrode, and then oxidize the aluminum to make the tunnel barrier [1-4]. We have produced nm-scale tunnel junctions in the useful resistance range in this way, but their reproducibility and our ability to control the magnetic properties of the electrodes adjacent to the tunnel barrier are still issues to be improved. Fig. 2(a) shows a conductance vs. voltage trace for a nm-scale junction made from cobalt/aluminum oxide/permalloy. The conductance increases as a function of bias, as expected due to spin excitations [2,4]. However, the hysteresis curves of the conductance as a function of applied magnetic field (Fig. 2(b)) suggest the presence of antiferromagnetic cobalt oxide in the junction region. Further experimental work is underway to eliminate this material and to understand more fully the microscopic nature of the magnetism in these and similar samples. The second strategy which we have begun to pursue (in collaboration with the chemist Chris Murray at IBM, Yorktown Heights) for making nm-scale magnetic tunnel junctions is to use self-assembled monolayers as the barrier material rather than oxides [5,6]. In work thus far, we have been able to produce a single-electron tunneling device containing a gold nanocluster surrounded by hexane-dithiol molecules, exhibiting a clear Coulomb-staircase current-voltage curve (Fig. 3). This indicates that these self-assembled monolayers have the ability to act as good tunnel barriers in our device geometry.

2. Summary of work to be performed in the next year

In the immediate future we will continue to study the nature of electron tunneling through individual nm-scale tunnel junctions made using deposited oxide barriers and self-assembled monolayer barriers. In this process, we expect to learn in some detail about the consequences of defects in magnetic tunnel junctions and about the microscopic nature of non-idealities in the coupling of magnetic electrodes across a tunnel barrier. We will also determine the optimal strategy for fabricating reliable tunneling transistors containing single magnetic nanoparticles. The need to take care with these materials issues was anticipated in our original proposal. Once this optimization is accomplished we plan to continue as outlined in the rest of our proposal, examining electron tunneling via the discrete quantum states within a magnetic nanoparticle.

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Students and postdocs associated with the project

Sophie Guéron, post-doc, supported from ONR funds
David Salinas, graduate student, supported from NSF-MRSEC funds
Ed Myers, graduate student, Dept. of Education fellowship
Stephan Meyer, undergraduate working part-time on software and electronics

Publications in this grant period:

D. C. Ralph, and V. Ambegaokar, "Conference Commentary on the Adriatico Research Conference on 'Superconductivity, Andreev Reflection, and Proximity Effect in Mesoscopic Structures'", to appear in *Comments on Condensed Matter Physics* **18** (cond-mat/9709230).

Invited talks:

1. "Superconducting Correlations and Their Breakdown within nm-Scale Aluminum Particles,"
Adriatico Research Conference -- Andreev Reflection and Proximity Effect in Mesoscopic Structures
July 8-11, 1997, Trieste, Italy.
2. "Interacting Electrons in a Box -- Tunneling Measurements of Electronic Energy Levels in Single Metal Particles,"
Adriatico Research Conference -- STM-Based Lithography and Atomic Electronics
July 15-18, 1997, Trieste, Italy.
3. "Effects of Electron Interactions on the Tunneling Spectra of Aluminum Nanoparticles",
Israeli Science Foundation Workshop -- Strong Interactions in Quantum Dots,
October 25-30, 1997, Dead Sea, Israel.
4. "Interacting Electrons in a Box -- Measurements of Electronic Energy Levels inside Single Metal Particles,"
William L. McMillan Prize Lecture
November 6, 1997, University of Illinois, Champaign-Urbana

Seminars at the University of Virginia, the National High Magnetic Field Laboratory, North Carolina State University, Michigan State University, and Princeton University.

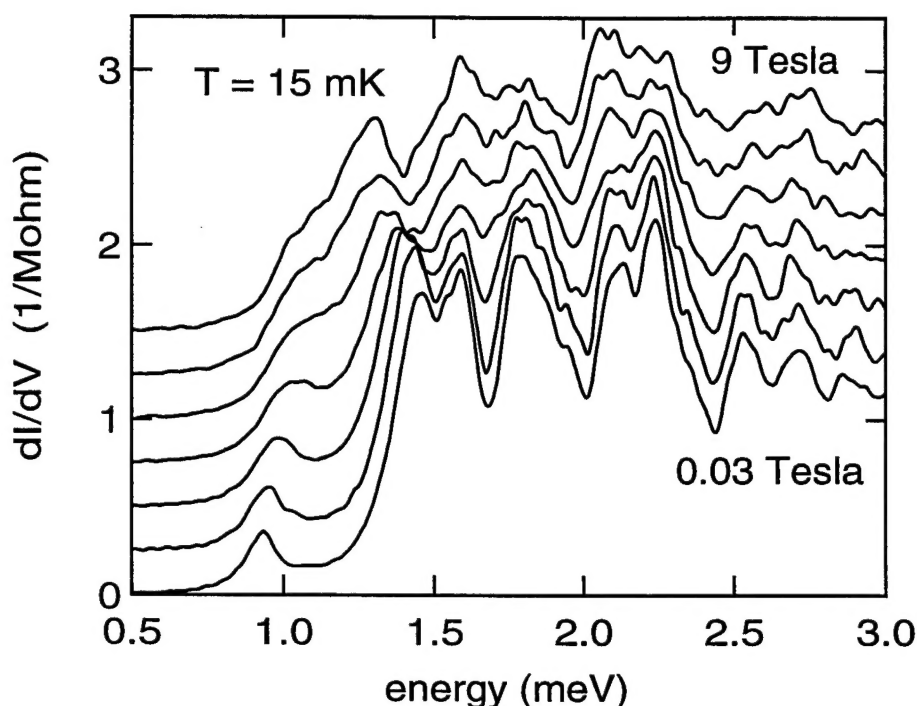


Fig. 1. Tunneling spectrum of discrete energy levels for a superconducting aluminum nanoparticle containing 4% gold impurities, for equally spaced increments of magnetic field from 0.03 to 9 Tesla. Achieving data of this quality was a successful test of our device fabrication and measurement systems.

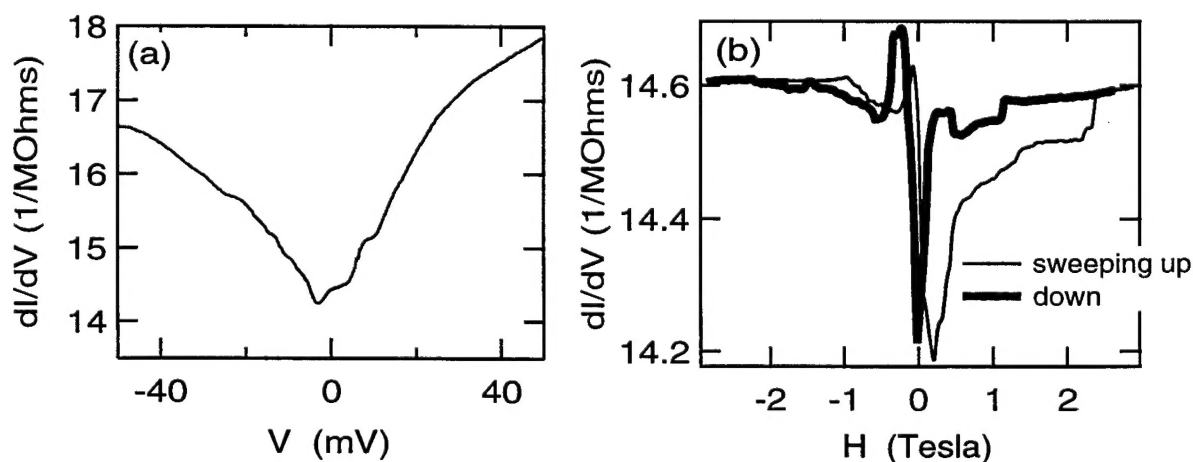


Fig. 2. Conductance of a nm-scale cobalt / oxidized aluminum / permalloy tunnel junction at a temperature of 4.2 K. (a) Zero-bias conductance minimum, as expected due to spin-wave assisted tunneling. (b) The complicated hysteresis curves and the large characteristic magnetic field scales indicate the probable existence of antiferromagnetic cobalt oxide in the junction region. Work is underway to optimize the fabrication of purely aluminum oxide barriers for the nm-scale junctions.

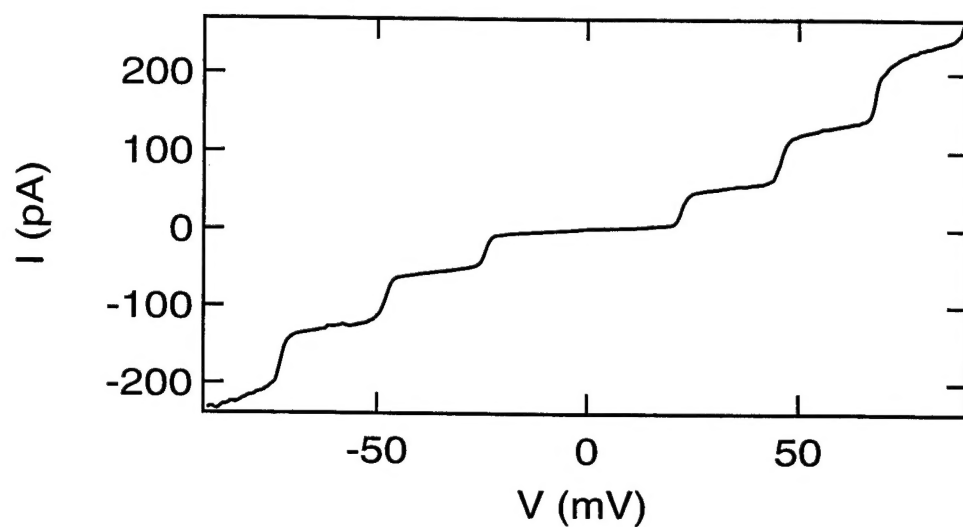


Fig. 3. "Coulomb staircase" current-voltage curve for electrons tunneling via a single gold nanoparticle in a device made with hexane-dithiol self-assembled-monolayer tunnel junctions. We are presently adapting the self-assembled monolayer technology for use with magnetic nanoparticles.